Density matrix $\boxed{\hat{\rho} = \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|} = \sum_n p_n |n\rangle\langle n|$ 1

$$\boxed{\langle \hat{O}\rangle = \mathrm{Tr}(\hat{O}\hat{\rho}) = \mathrm{Tr}(\hat{\rho}\hat{O})}$$

$$\boxed{i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]} \Rightarrow \text{steady state } \hat{\rho} = f(\hat{H})$$

Canonical: $p_n = \frac{1}{Z} e^{-\beta E_n} \Leftrightarrow \hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$

$$Z = \mathrm{Tr}(e^{-\beta\hat{H}}) = \sum_n e^{-\beta E_n}$$

Grand canonical: $\hat{\rho} = \frac{1}{Q} e^{-\beta\hat{H} + \beta\mu\hat{N}}$; $Q(\beta,\mu) = \mathrm{Tr}\left(e^{-\beta\hat{H}+\beta\mu\hat{N}}\right)$

6.2) A particle in a box

$$H = \frac{\hat{p}^2}{2m} \; ; \; \langle x|\hat{p}|\psi\rangle = -i\hbar\vec{\nabla}\langle x|\psi(x)\rangle$$

$H|\psi\rangle = \lambda|\psi\rangle \Rightarrow -\frac{\hbar^2}{2m}\Delta\langle x|\psi\rangle = \lambda\langle x|\psi\rangle$ & $\langle x|\psi\rangle = \psi(x)$ periodic

$\Rightarrow |\psi\rangle = |\vec{k}\rangle$, with $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ & $\langle x|k\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{x}}$

Then $H|\vec{k}\rangle = \varepsilon(\vec{k})|\vec{k}\rangle$ with $\varepsilon(\vec{k}) = \frac{\hbar^2\vec{k}^2}{2m} = \frac{\vec{p}^2}{2m}$ with $\vec{p} = \hbar\vec{k}$

Partition function

$$Z = \mathrm{Tr}(e^{-\beta\hat{H}}) = \sum_{\vec{k}} e^{-\beta\frac{\hbar^2 k^2}{2m}} = \frac{V}{(2\pi)^3}\int d^3\vec{k}\, e^{-\beta\frac{\hbar^2 k^2}{2m}} = \frac{V}{(2\pi)^3}\sqrt{\frac{8\pi m k_B T}{\hbar^2}} = \frac{V}{\lambda^3}$$

We recover the classical stat mech result!

Density matrix

$$\langle x'|\hat{\rho}_c|x\rangle = \sum_{\vec{k}} \frac{e^{-\beta\varepsilon(\vec{k})}}{Z} \langle x'|k\rangle\langle k|x\rangle = \frac{\Lambda^3}{V}\frac{\cancel{V}}{(2\pi)^3}\int d^3\vec{k}\, e^{-\beta\frac{\hbar^2\vec{k}^2}{2m}} \frac{e^{-i\vec{k}\cdot(\vec{x}'-\vec{x})}}{\cancel{V}}$$

$$= \frac{1}{V}\exp\left[-\frac{\pi(\vec{x}-\vec{x}')^2}{\Lambda^2}\right] \text{ where we used } \beta\frac{\hbar^2}{m} = \frac{1}{2\pi}\frac{h^2}{2\pi m k_B T} = \frac{\Lambda^2}{2\pi}$$

(i) $\langle x|\hat{\rho}_c|x\rangle = \frac{1}{V}$, as expected

(ii) The statistical mixture is coherent over a scale $|\vec{x}-\vec{x}'| \sim \Lambda$

$\Rightarrow$ the thermal de Broglie wavelength measures the coherence length of the thermal mixture.

$\Rightarrow$ At temperature T, the particle is a wave packet spread over Λ

6.3) Quantum gases

To characterize the statistical properties of a system, we thus need to build $\hat{\rho} = \sum_n f(E_n)|n\rangle\langle n| \Rightarrow$ find $|n\rangle$

Symmetry properties:

If particles are indistinguishable, $P(x_1, x_2, \dots, x_N) = P(x_2, x_1, \dots, x_N)$

$$\Leftrightarrow |\psi(x_1, x_2, \dots, x_N)|^2 = |\psi(x_2, x_1, \dots, x_N)|^2 \Rightarrow \boxed{\psi(x_2, x_1, \dots, x_N) = e^{i\theta}\psi(x_1, x_2, \dots, x_N)}$$

Swapping x_1 & x_2 twice leads back to $x_1, x_2, \dots, x_N \Rightarrow e^{2i\theta} = 1$ & $\boxed{\theta = 0 \text{ or } \pi}$

Spin statistics theorem [Pauli, Phys Rev 58, 716, (1940)]

Particles with intrinsic spins s are such that

s integer $\Leftrightarrow$ bosons & $\theta=0$ $\Rightarrow$ ψ fully symmetric

s half-integer $\Leftrightarrow$ fermions & $\theta=\pi$ $\Rightarrow$ ψ fully antisymmetric

Eigenstates

* Denote $|h\rangle$ the eigenstates of 1 particle.

Non interacting gas: $|h_1 \dots h_N\rangle = |h_1\rangle \otimes |h_2\rangle \otimes \dots \otimes |h_N\rangle$ forms a basis of the full Hilbert space, without any particular symmetry.

* We introduce $\eta = 1$ (or "+") for bosons & $\eta=-1$ (or "−") for fermions

* The properly symmetrized eigenstate is

$$\boxed{|\psi\rangle_\eta = \frac{1}{\sqrt{N_\eta}} \sum_{\sigma \in \mathfrak{S}(N)} (\eta)^{p(\sigma)} \, |h_{\sigma(1)} - h_{\sigma(N)}\rangle} \qquad (*)$$

→ $\mathfrak{S}(N)$ is the group of permutations of $\{1, \dots, N\}$

→ $p(\sigma)$ is the parity of the permutation σ (= # of pairwise swap to go from $1, -, N$ to $\sigma(1), -, \sigma(N)$).

→ N_η is a normalization such that ${}_\eta\langle\psi|\psi\rangle_\eta = 1$

Normalization:

$${}_\eta\langle\psi|\psi\rangle_\eta = \frac{1}{N_\eta} \sum_{\sigma_1,\sigma_2} \eta^{p(\sigma_1)+p(\sigma_2)} \underbrace{\langle h_{\sigma_1(1)} - h_{\sigma_1(N)} | h_{\sigma_2(1)} - h_{\sigma_2(N)}\rangle}_{\langle h_{\sigma_1(1)}|h_{\sigma_2(1)}\rangle \cdots \langle h_{\sigma_1(N)}|h_{\sigma_2(N)}\rangle}$$

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Bosons σ_2 is a permutation of $(1,\dots,N)$ but also of $(\sigma_1(1),\dots,\sigma_1(N))$

$$\prod_i \langle h_{\sigma_1(i)} | h_{\sigma_2(i)} \rangle = \prod_j \langle h_j | h_{\tilde{\sigma}_2(j)} \rangle \quad \& \quad \sum_{\sigma_1}\sum_{\sigma_2} \to N! \sum_{\tilde{\sigma}_2}$$

$$\langle\psi|\psi\rangle_+ = \frac{N!}{N_+} \sum_{\tilde{\sigma}_2} \underbrace{\langle h_1 | h_{\tilde{\sigma}(1)}\rangle \dots \langle h_N | h_{\tilde{\sigma}(N)}\rangle}_{\neq 0 \text{ iff } \tilde{\sigma}(i)=i\,;\ =1 \text{ otherwise}}$$

If there are n_h bosons in state $|h\rangle$, there are $\prod_h (n_h)!$ such permutations.

$$\Rightarrow \boxed{N^+ = N! \prod_h (n_h)!}$$

Fermions If there are two particles i & j in the same state $(h_i = h_j)$, we can introduce $\tilde{\sigma} = \sigma \circ (i \leftrightarrow j)$. Then $|h_{\sigma(1)} - h_{\sigma(N)}\rangle = |h_{\tilde{\sigma}(1)} - h_{\tilde{\sigma}(N)}\rangle$

$$|\psi\rangle_- = \frac{1}{2\sqrt{N^-}} \sum_\sigma \left[(-1)^{P(\sigma)} |h_{\sigma(1)} - h_{\sigma(N)}\rangle + \underbrace{(-1)^{P(\sigma)}}_{-(-1)^{P(\tilde{\sigma})}} |h_{\tilde{\sigma}(1)} - h_{\tilde{\sigma}(N)}\rangle \right]$$

$$= \frac{1}{2\sqrt{N^-}} \left[\sum_\sigma (-1)^{P(\sigma)} |h_{\sigma(1)} - h_{\sigma(N)}\rangle - \underbrace{\sum_\sigma}_{=\sum_{\tilde{\sigma}}} (-1)^{P(\tilde{\sigma})} |h_{\tilde{\sigma}(1)} - h_{\tilde{\sigma}(N)}\rangle \right] = 0$$

$\Rightarrow$ Eigenstates with two fermions in the same state vanish!

Then $\langle h_{\sigma_1(1)} — h_{\sigma_1(N)} | h_{\sigma_2(1)} — h_{\sigma_2(N)}\rangle = 0$ if $\sigma_1 \neq \sigma_2$ & $N^- = N!$

Since $n_h = 0$ or 1, $N^- = N! \prod_h (n_h)!$ also true!

All in all
$$\boxed{|\psi\rangle_\eta = \frac{1}{\sqrt{N! \prod_h (n_h)!}} \sum_{\sigma \in S(N)} \eta^{P(\sigma)} |h_{\sigma(1)} — h_{\sigma(N)}\rangle}$$

This looks complicated but makes life simpler than in classical stat mech.

* classical stat mech: state defined by $\sigma_1, \dots, \sigma_N$ and, if need be, we replace $\sum_{\sigma_1,\dots,\sigma_N} P(\sigma_1,\dots,\sigma_N)$ by $\frac{1}{N!}\sum_{\sigma_1,\dots,\sigma_N} P(\sigma_1,\dots,\sigma_N)$ to avoid overcounting $\Rightarrow$ source of confusion

* Quantum stat mech: the eigenstate is always correctly symmetrized $\Rightarrow$ only ONE state with n_k particles in $|k\rangle$

$$\Rightarrow \mathrm{Tr}\left(e^{-\beta \hat{H}}\right) = \sum_{\{\sum_k n_k = N\}} e^{-\beta \sum_k n_k \varepsilon_k} \quad ; \ \varepsilon_k \text{ energy levels}$$

$\Rightarrow$ No need to correct anything, the trace includes what's needed.

Still, the constrained sum such that $\sum_k n_k = N$ is hard $\Rightarrow$ grand canonical

Grand canonical partition function

$$Q = \mathrm{Tr}\left(e^{-\beta\hat{H} + \beta\mu\hat{N}}\right) = \sum_{\{n_k\}} e^{\beta\mu \sum_k n_k - \beta \sum_k n_k \varepsilon_k} = \prod_k \sum_{\{n_k\}} \left[e^{\beta(\mu - \varepsilon_k)}\right]^{n_k}$$

Fermions: $n_k = 0, 1$ $\quad \boxed{Q_- = \prod_k \left(1 + e^{\beta(\mu - \varepsilon_k)}\right)}$

Bosons: $n_k \in \mathbb{Z}^+$ $\quad \boxed{Q_+ = \prod_k \frac{1}{1 - e^{\beta(\mu - \varepsilon_k)}}}$

$$\boxed{Q_\eta = \prod_k \left[1 - \eta e^{\beta(\mu - \varepsilon_k)}\right]^{-\eta}}$$

Bosons require $\mu < \varepsilon_0$ for convergence of Q_+.

Then $$\boxed{P_\eta(\{n_k\}) = \frac{1}{Q_\eta} \prod_k e^{\beta(\mu-\varepsilon_k)n_k}}$$

Occupation statistics

$$\boxed{\langle n_k \rangle = -\frac{1}{\beta}\,\partial_{\varepsilon_k} \ln Q_\eta = \frac{e^{\beta(\mu-\varepsilon_k)}}{1-\eta\, e^{\beta(\mu-\varepsilon_k)}} = \frac{1}{e^{\beta(\varepsilon_k-\mu)}-\eta}}$$